



Carbon xerogels and ceria–carbon xerogel materials as catalysts in the ozonation of organic pollutants

C.A. Orge, J.J.M. Órfão, M.F.R. Pereira*

Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:

Received 3 May 2012

Received in revised form 25 June 2012

Accepted 29 June 2012

Available online 6 July 2012

Keywords:

Catalytic ozonation

Cerium oxide

Carbon xerogel

Oxalic acid

Textile dye

ABSTRACT

Carbon xerogels prepared at different pH and ceria–carbon xerogel materials with different compositions and synthesized by different procedures were evaluated as catalysts in the ozonation of oxalic acid and the textile dye CI Reactive Blue 5. The prepared samples were characterized by N₂ adsorption at −196 °C, X-ray diffraction and scanning electronic microscopy. All the catalysts containing both cerium oxide and carbon xerogel removed all oxalic acid in solution after 1 h of reaction. Cerium oxide supported on carbon xerogel and carbon xerogel containing 1% of cerium oxide prepared by one-pot synthesis were the most active catalysts for the ozonation of the dye solution. Considering the catalytic activity and the steps involved in the preparation of materials, the carbon xerogel containing 1% of cerium oxide prepared by one-pot synthesis is the most promising catalyst.

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1. Introduction

Ozone is widely used in water treatment as disinfectant and oxidant. Transformation of organic compounds occurs via direct reaction with ozone or indirectly with hydroxyl radicals (HO•), resulting from ozone decomposition in water [1]. Ozone reacts selectively with organic compounds attacking preferentially aromatic rings and unsaturated bonds, whereas HO• is a less selective and more powerful oxidant. Despite several advantages of using ozone, there are a few disadvantages that limit its application in water treatment, such as the cost of generation and its highly selective oxidation power [2]. In order to overcome the latter problem, some ozone-based advanced oxidation processes have been developed; among them catalytic ozonation has received wide interest as a promising technology for removing refractory organic pollutants in water. Ozone combined with appropriate catalysts can improve the removal of taste, colour and organic contaminants.

Porous carbon materials prepared by polycondensation of hydroxylated aromatics (phenol, catechol, resorcinol, hydroquinone or phloroglucinol) and aldehydes (formaldehyde or furfural) in a solvent followed by drying and pyrolysis have been

extensively studied [3]. The nature of the precursors, the gelation conditions and the drying method determine the texture of the carbon material obtained. For the preparation of carbon xerogels the most common precursors are resorcinol and formaldehyde, and the polymer is usually synthesized using water as solvent and Na₂CO₃ as catalyst. Carbon xerogels present excellent properties, such as high specific surface area, porosity and conductivity, controllable average pore size and they can be prepared in the desired form (monolith, thin film and powder) [4].

An extended mineralisation was observed when Mn, Co or Ce oxides supported on activated carbon were used in the ozonation of sulphanic acid, aniline and a reactive dye [5]. The association of ozone and carbon xerogels with different surface chemical properties was reported in a previous study [6], and an improvement of the TOC removal from dye solutions was observed, especially with the more basic material. In a recent work, the effect of the composition and the influence of the surface chemistry and textural properties of carbon materials in the catalytic activity of ceria–carbon composites were evaluated. It was concluded that ceria–carbon xerogel composites presented better performance than carbon xerogel in the ozonation of oxalic acid [7].

The aim of this work is to study the ozonation of selected organic pollutants (oxalic acid and the textile dye CI Reactive Blue 5) in the presence of carbon xerogels with different properties, and ceria–carbon xerogel materials with different compositions and synthesized by different procedures (incipient wetness method, one-pot synthesis and precipitation method).

* Corresponding author. Tel.: +351 225081468; fax: +351 225081449.

E-mail addresses: carla.orge@fe.up.pt (C.A. Orge), jjmo@fe.up.pt (J.J.M. Órfão), fpereira@fe.up.pt (M.F.R. Pereira).

Table 1
Properties of the prepared samples.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	$d_{\text{BJH}}^{\text{a}}$ (nm)	d_{p} (nm)
XC.pH = 6.25	540	168	0.192	3.2	–
XC.pH = 6.0	588	241	0.176	4.1	–
XC.pH = 5.45	566	233	0.165	24.4	–
1%Ce/XC.in situ	510	244	0.137	14.1	–
1%Ce/XC.supported	547	237	0.158	24.2	–
5%Ce/XC.supported	559	250	0.156	24.5	8.3 ^b
10%Ce/XC.supported	558	249	0.159	25.9	9.2 ^b
10%Ce/90%XC	573	228	0.174	24.3	3.6 (77.8%); 46 (22.2%) ^c

^a Average mesopore diameter obtained by the Barret, Joyner and Halenda (BJH) method applied to the desorption isotherm.

^b Crystallite diameters of CeO_2 determined by XRD analyses.

^c XRD analyses using Rietveld refinement and the relative amount of each grain size.

2. Experimental

2.1. Materials and characterisation methods

Two organic molecules were selected for this study: oxalic acid (99%, Sigma–Aldrich) and a textile dye (CI Reactive Blue 5).

Different sets of catalysts were prepared. The first one consists of carbon xerogels prepared by the sol–gel process at different initial pH (identified as XC.pH = 5.45, XC.pH = 6.0 and XC.pH = 6.25). The second set of catalysts correspond to cerium oxide supported by the incipient wetness method on the carbon xerogel synthesized at pH 5.45, with 1, 5 and 10 wt% of CeO_2 (samples 1%Ce/XC.supported, 5%Ce/XC.supported and 10%Ce/XC.supported, respectively). In the scope of the present investigation, a novel catalyst with 1 wt% of cerium oxide was also prepared by one-pot synthesis (1%Ce/XC.in situ). Finally, a composite with 10% of cerium oxide and 90% of the carbon xerogel prepared at pH 5.45 was synthesized by the precipitation method as described in a previous work [7] (sample 10%Ce/90%XC).

The synthesis of the carbon xerogel consisted in the polycondensation of resorcinol (99%, Aldrich) with formaldehyde (37%, Aldrich), at an initially controlled pH [3,4,8]. Carbon xerogels prepared at pH 5.45, 6.0 and 6.25 were synthesized in order to obtain materials with different textural properties. After setting the pH of the sol–gel process with NaOH solutions, polymerisation was carried out at 85 °C during 3 days. Then, the gel was ground and dried in an oven during 4 days (first day at 60 °C, second day at 80 °C, third day at 100 °C and fourth day at 120 °C). Finally, the material was carbonised under nitrogen flow at 800 °C using the following temperature program: from room temperature to 150 °C (hold 2 h) at 2 °C min^{−1}, 2 °C min^{−1} to 400 °C (hold 1 h), 2 °C min^{−1} to 600 °C (hold 1 h), 2 °C min^{−1} to 800 °C (hold 6 h) and cooling down to room temperature.

Ceria supported on carbon xerogel materials were prepared by the incipient wetness method from cerium nitrate solutions in order to obtain the contents of cerium oxide mentioned above. After drying at 100 °C for 24 h, the samples were thermally treated in N_2 (50 cm³ min^{−1}) at 400 °C for 1 h.

The ceria–carbon xerogel prepared by one-pot synthesis was obtained by a procedure similar to that described for the carbon xerogel at pH 5.45, but resorcinol and formaldehyde were dissolved in water containing cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), in which concentration was calculated in order to obtain 1 wt% of cerium oxide in the prepared material. This synthesis was ceria–carbon xerogels with 5 and 10 wt% of cerium oxide were also prepared by one-pot synthesis. However, after characterisation, it was possible to conclude that the introduction of large amounts of cerium nitrate before polymerisation destroys the carbon xerogel structure. Thus, these materials were not considered in this study.

The textural characterisation of the materials was based on the corresponding N_2 equilibrium adsorption/desorption isotherms,

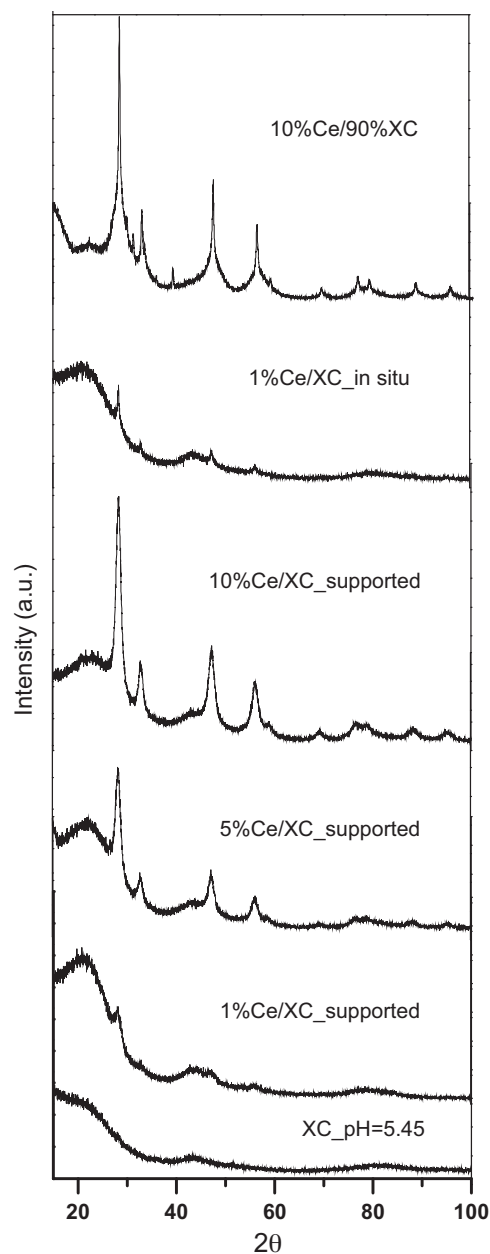


Fig. 1. X-ray diffractograms of carbon xerogel XC.pH = 5.45 and ceria–carbon xerogel materials.

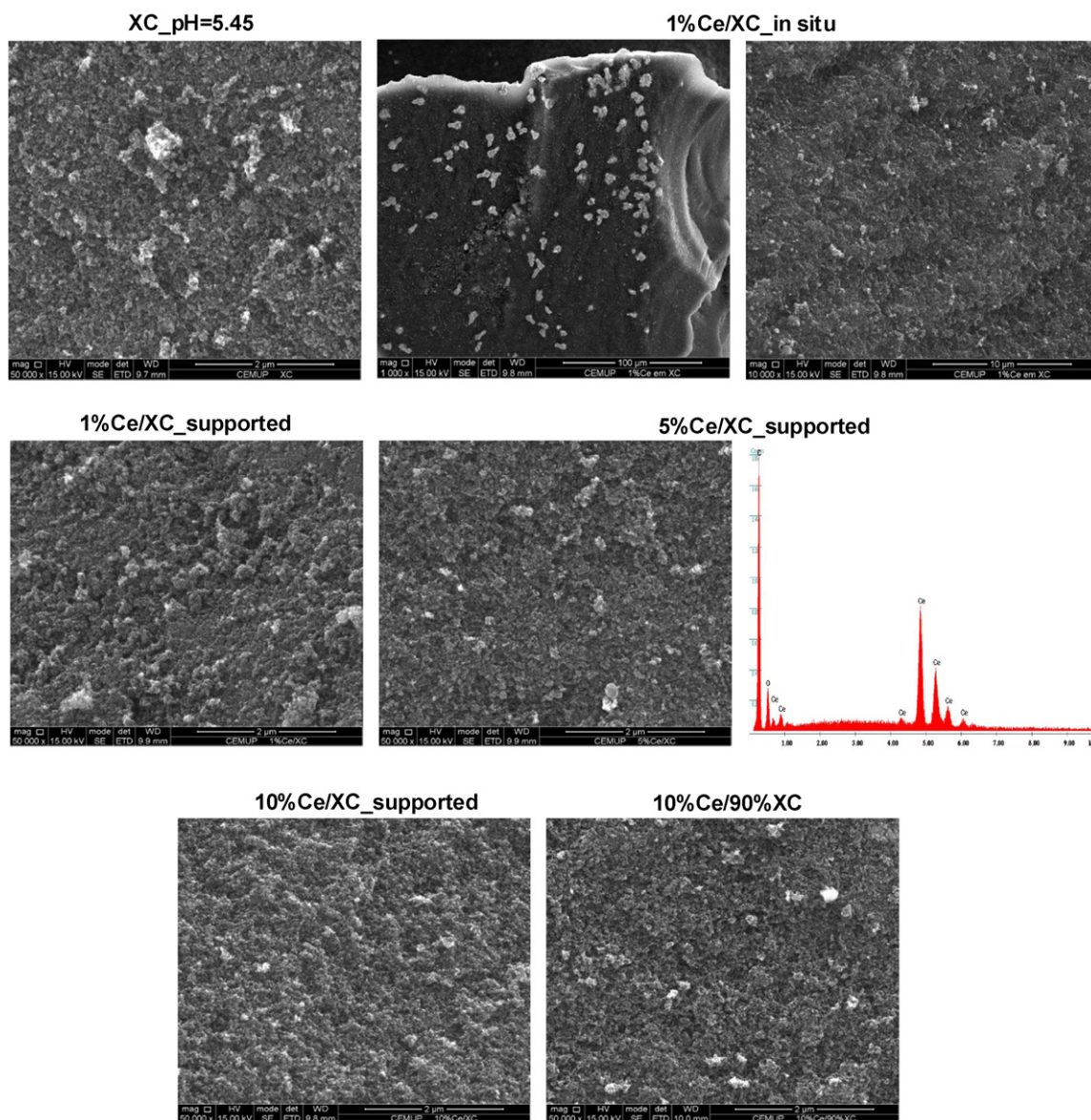


Fig. 2. SEM images of the prepared materials and EDS analysis of the sample 5%Ce/XC_supported.

determined at -196°C with a Quantachrome Instruments NOVA 4200e apparatus. BET surface areas (S_{BET}), mesoporous surface areas ($S_{\text{mesopores}}$), micropore volumes ($V_{\text{micropores}}$) and average mesopore diameters obtained by the Barret, Joyner and Halenda (BJH) method were calculated. The relative amount of cerium oxide in the catalyst was determined by thermo gravimetric analysis under air in a STA 409 PC/4/H Luxx Netzsch thermal analyser. The morphology and the semi-quantitative elemental analysis of the catalysts were obtained by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively, in a JEOL JSM 35C/Noran Voyager system. XRD spectra were recorded on a Philips X'Pert MPD diffract meter ($\text{Cu K}\alpha = 0.15406 \text{ nm}$).

2.2. Kinetics experiments

The removal of pollutants was investigated in a slurry lab-scale reactor equipped with agitation. In each experiment the reactor was filled with 700 cm^3 of pollutant solution ($C_{0,\text{oxalic acid}} = 1 \text{ mM}$, $C_{0,\text{dye}} = 100 \text{ mg L}^{-1}$) at the natural pH ($\text{pH}_{0,\text{oxalic acid}} \approx 3.0$, $\text{pH}_{0,\text{dye}} = 5.5$). Single ozonation and adsorption experiments were also carried out under similar conditions

for comparison purposes. In adsorption and catalytic ozonation experiments, 350 mg of catalyst (particle size = $100\text{--}300 \mu\text{m}$) were introduced in the reactor. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant total gas flow rate ($150 \text{ cm}^3 \text{ min}^{-1}$) and constant inlet ozone concentration (50 g m^{-3}). The concentration of ozone in the gas phase was monitored with a BMT 964 ozone analyser. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with potassium iodide solution. A stirring rate of 400 rpm was used in order to keep the reactor content perfectly mixed. In the adsorption tests, the ozone-containing stream was replaced by an oxygen stream. In the experiments carried out in the presence of *tert*-butanol, a concentration of 10 mM of this radical scavenger was used [9].

The concentration of oxalic acid was followed by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was an Aminex HPX-87H column ($300 \text{ mm} \times 7.8 \text{ mm}$) working at room temperature under isocratic elution with H_2SO_4 4 mM . Dye solution decolourisation was followed by UV-vis spectrophotometry with a JASCO V-560 UV/Vis spectrophotometer at the maximum absorption

wavelength (597 nm), previously determined. The degree of mineralisation was followed by total organic carbon (TOC) analysis in a Shimadzu TOC-5000A equipment.

3. Results and discussion

3.1. Characterisation of the catalysts

The properties of the prepared materials are presented in Table 1.

The main differences among the carbon xerogels (XC) prepared at different initial pH are in the average mesopore diameter. The carbon xerogel prepared at pH 5.45 has the largest mesopore sizes ($d_{\text{BJH}} = 24.4$ nm). The catalysts of cerium oxide supported on carbon xerogel and the composite present similar textural properties. The sample 1%Ce/XC.in situ has a specific surface area and an average mesopore diameter smaller than XC pH 5.45.

Fig. 1 shows the X-ray diffraction patterns of the prepared catalysts. According to the results, the dominant diffraction peaks are those characteristic of cerianite (CeO_2). The intensity of peaks in samples 1%Ce/XC.in situ and 1%Ce/XC.supported is low, since these catalysts only have 1 wt% of cerium oxide. Besides cerianite, the 10%Ce/90%XC composite also has secondary phases, which are identified by small peaks at 31.5° , 36° and 39° . Since this sample presents wide peaks, it is necessary to apply a model of two characteristic particle sizes (Rietveld refinement), instead of a model with a single particle size distribution. The values of crystallite diameters and the relative amount of each grain size are presented in Table 1. The 10%Ce/90%XC sample presents two different average sizes, i.e. particles with 3.6 and 46 nm, small particles being predominant. No significant differences between the crystallite diameters of the cerium oxide supported on carbon xerogel materials were observed (Table 1).

The morphology of the synthesized materials was examined by SEM and some representative images are depicted in Fig. 2. Analyses of EDS were also performed (spectrum obtained with sample 5%Ce/XC.supported is included in Fig. 2 as an example) with the aim of evaluating the presence of cerium in the prepared samples. Carbon xerogel and ceria–carbon xerogel materials present similar morphologies.

3.2. Kinetic results

3.2.1. Oxalic acid removal

Oxalic acid was selected for this study because it remains in solution after non-catalytic ozonation processes due to its high refractory character [10]. Fig. 3 shows the results obtained for oxalic acid degradation by single ozonation and catalytic ozonation in the presence of the prepared materials. The kinetic results obtained with cerium oxide prepared by the precipitation method (Ce–O) were also included [7].

The addition of any of the prepared materials resulted in better performance than single ozonation and ozonation catalysed by cerium oxide, a total removal being achieved after 1 h of catalytic ozonation. The carbon xerogel prepared at pH 6.25 showed a better performance than the other carbon xerogels, but no differences were observed between the carbon xerogels prepared at pH 6.0 and 5.45. The addition of cerium oxide to the carbon xerogel increased the catalytic activity, regardless of the preparation method. Ceria supported on carbon xerogel with more cerium oxide presented the best performance. No significant differences between catalysts with 1% of cerium oxide prepared by one-pot synthesis and prepared by the incipient wetness method were observed. The performance verified for the composite (10%Ce/90%XC) is slightly lower than that observed in the ozonation catalysed by 10% of cerium oxide supported on the carbon xerogel sample.

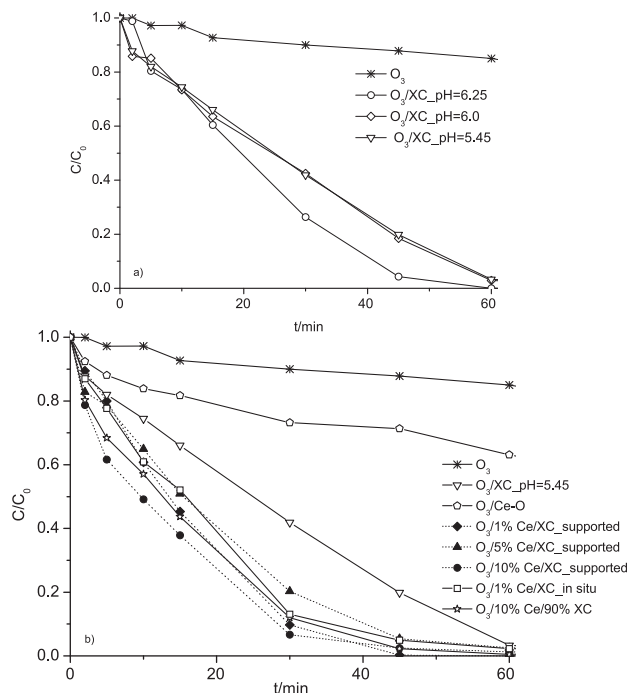


Fig. 3. Evolution of the dimensionless concentration of oxalic acid during single ozonation and ozonation catalysed by carbon xerogels prepared at different pH (a) and by cerium oxide and ceria–carbon xerogel materials (b).

The absence of internal and external diffusional limitations was experimentally confirmed because there was no increase in the performance of the catalysts using smaller particles ($d_p < 50$ mm) or higher stirring rates (700 rpm), respectively [11].

3.2.2. Reactive dye removal

Textile industries are responsible for the discharge of large quantities of dyes into natural waterways due to inefficiencies in dyeing techniques [12]. Up to 50% of dyes are lost directly into watercourses when using reactive dyes [13]. The presence of dyes in the effluent, even at very low concentrations, could be highly visible and undesirable [14]. Coloured wastewater influences negatively the aesthetic nature of water and reduces light penetration through the water's surface, and also the photosynthetic activity of aquatic organisms. Moreover, textile wastewater contains toxic and potential carcinogenic substances and therefore they must be adequately treated [15]. There are several treatment methods that can be applied to textile effluents, involving biological, physical or chemical processes; however, conventional biological wastewater treatment methods are ineffective in removing the colour. On the contrary, ozone is frequently used for decolourising dye wastewater because it attacks, preferentially, aromatic structures and unsaturated bonds, such as dye chromophores, which are responsible for the colour.

Fig. 4 presents the kinetic results of single and catalytic ozonation of the dye CI Reactive Blue 5. Total decolourisation is attained in less than 30 min when ozone is applied, and this time is practically independent of the presence of the catalysts. Single ozonation also originates a decrease in the concentration of TOC in solution; nevertheless, mineralisation occurs at a much lower rate than colour removal, which means that part of the dye degradation products (colourless) still remains in solution. The advantage of using a catalyst is clearly seen in the TOC removal, which is faster than that corresponding to single ozonation. In Fig. 4a it is possible to verify that the catalytic activity of the carbon xerogels increases when the pH used in the preparation process decreases. This result may

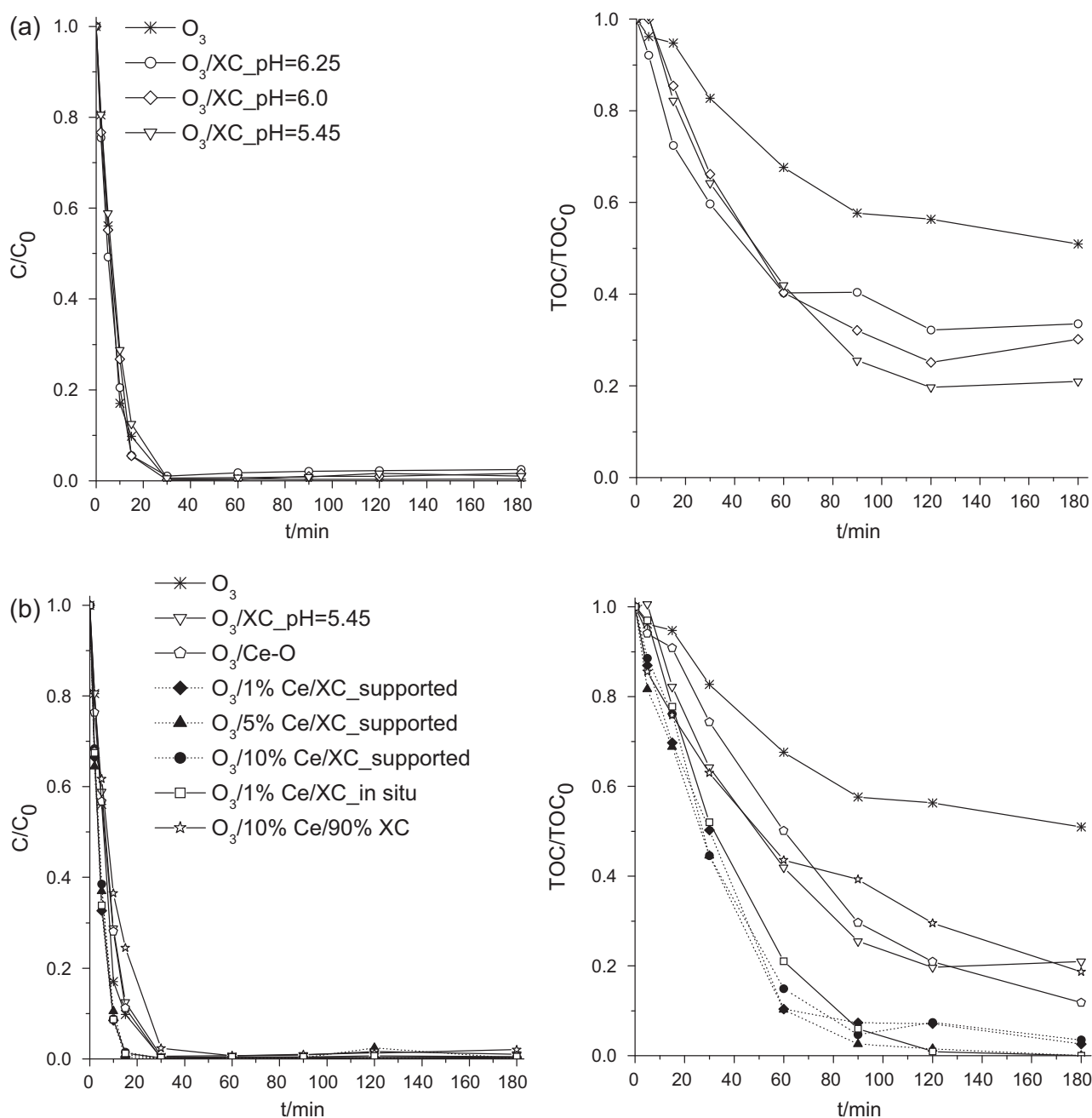


Fig. 4. Colour and TOC removal for the reactive dye during single ozonation, and ozonation catalysed by carbon xerogels prepared at different pH (a) and by cerium oxide and ceria-carbon xerogel materials (b).

be explained by the larger mesopores obtained in the preparation at lower pH (see Table 1), which may allow an easier access of the dye, a bulky molecule, and primary degradation compounds to the interior of the pores.

With the exception of the composite prepared by the precipitation method, all catalyst containing cerium oxide and carbon xerogel showed better performances than the carbon xerogel prepared at pH 5.45, and a complete mineralisation was achieved after 2–3 h of reaction. The catalysts of cerium oxide supported on carbon xerogel had a similar performance, regardless of the amount of cerium oxide present. The catalysts prepared by one-pot synthesis (1%Ce/XC *in situ*) led to total mineralisation after 2 h of reaction. It is possible to conclude that the introduction of cerium in the carbon xerogel, before or after polymerisation, is very efficient for the complete mineralisation of the reactive dye.

3.3. Considerations on the reaction mechanism and catalyst stability

In order to study if the ozonation of oxalic acid in the presence of the prepared catalysts involves HO^\bullet radicals in the liquid phase, experiments of oxalic acid ozonation with 1%Ce_XC_supported, 1%Ce_XC_in situ and 10%Ce/90%XC were carried out in the presence of *tert*-butanol, a well known HO^\bullet radical scavenger. Adsorption kinetics of oxalic acid were also determined on the same samples. The results obtained are presented in Fig. 5. The results show that ozonation catalysed by 1%Ce_XC_supported or by 1%Ce_XC_in situ is practically not affected by the presence of *tert*-butanol, which indicates that the oxidation of oxalic acid does not occur via HO^\bullet radicals in the liquid bulk. On the other hand, a slight decrease in the catalytic ozonation of oxalic acid in the presence of *tert*-butanol

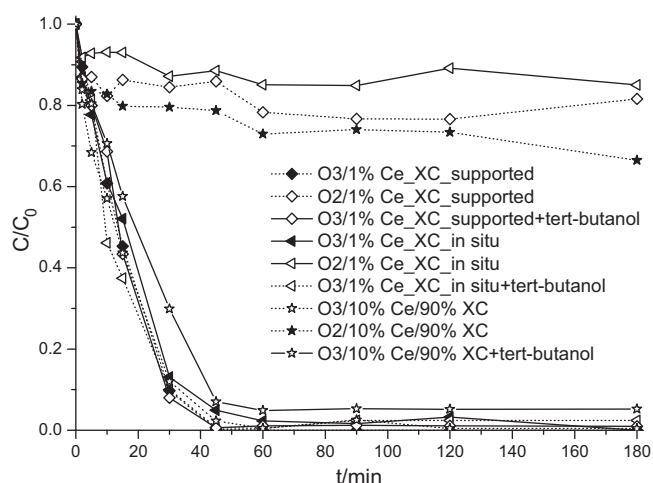


Fig. 5. Evolution of the dimensionless concentration of oxalic acid during adsorption, catalytic ozonation and effect of *tert*-butanol ($C_{\text{tert-butanol}} = 10 \text{ mM}$).

was observed when the ceria-activated carbon composite was used. In a previous work, where composites of cerium oxide and carbon materials were evaluated, a similar performance was observed, and it was suggested that oxalic acid is oxidized mainly on the surface of the composite, which is due to the contribution of the carbon material [7]. Adsorption on 10%Ce/90%XC composite allowed an oxalic acid removal slightly higher than that verified with the other catalysts, the process being able to remove 34% after 3 h. Therefore, it is possible to conclude that organic compounds and ozone can adsorb and react on the surface of catalysts. Since the oxidation of oxalic acid in the presence of the prepared materials does not occur, at least significantly, by bulk reactions involving HO^\bullet radicals, it is believed that the reaction mechanism comprises predominantly surface reactions.

With the aim of evaluating the eventual deactivation of the prepared materials during the ozonation experiments, five consecutive runs with sample 5%Ce/XC_supported were carried out with fresh oxalic acid solutions. The kinetic results presented in Fig. 6 show that there is a significant decrease of the catalytic activity from the first to third run. After the fourth run no important differences were observed, and a complete oxalic acid mineralisation was achieved after 90 min of reaction. According to the literature, the catalysts suffer a slight progressive oxidation by exposure to dissolved ozone and consequently the amount of oxygenated groups

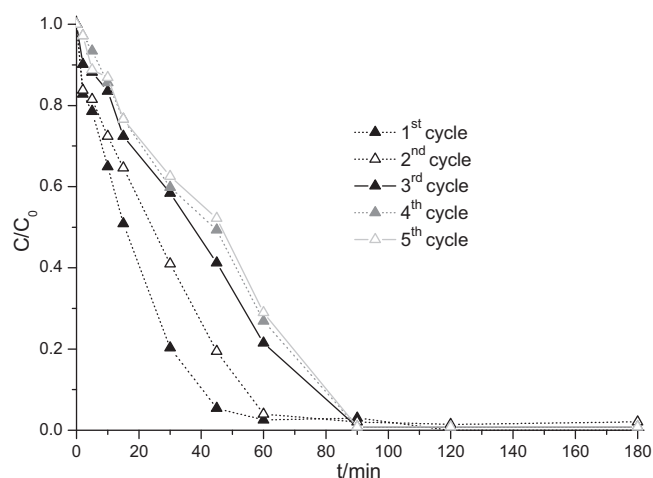


Fig. 6. Evolution of the dimensionless concentration of oxalic acid in successive experiments with the 5%Ce_XC_supported sample.

increases [16]. The amount of free electrons available on the catalyst surface decreases, since most of the oxygenated groups have the capacity of attracting them [17]. Then, the decrease observed in the activity of this sample in successive runs might be due to the introduction during reaction of electron-withdrawing oxygenated groups that reduce the electron density on the carbon basal planes. The role of the mentioned free electrons on the reaction mechanism was discussed elsewhere [7,10,18,19] for different ceria and carbon containing catalysts.

3.4. Selection of the best catalyst

In order to select the best catalyst it is necessary to evaluate several parameters. Considering the catalytic activity, as well as the time used in the preparation of the studied catalysts and the cost associated, the catalyst with 1 wt% of cerium oxide prepared by one-pot synthesis (1%Ce/XC_in situ) seems to be the best option. Although samples 1%Ce/XC_in situ and 1%Ce/XC_supported did not present different activities, the preparation of the catalyst of cerium oxide supported on carbon xerogel is longer and costly. Synthesis of ceria-supported on carbon xerogel requires two steps: preparation of carbon xerogel and ceria impregnation. Then, a carbonisation of carbon xerogel and a final thermal treatment are necessary. On the other hand, 1%Ce/XC_in situ is prepared in one step, since the cerium precursor is introduced during the preparation of the carbon material, which requires less time and only one thermal treatment. Comparing with the composite, the sample prepared by one-pot synthesis remains the best material. In the case of oxalic acid, no significant differences were observed, but in the dye degradation the composite had a worse performance. In addition to the synthesis of the composite being performed in two steps, which requires two thermal treatments, the amount of cerium precursor necessary to obtain the composite was larger, and therefore its preparation is more expensive.

4. Conclusions

Carbon xerogels with different textural properties and ceria-carbon xerogels materials with different compositions and synthesized by different routes were tested in the ozonation of oxalic acid and a reactive dye.

Pore sizes of carbon xerogels play a key role in the degradation of the selected pollutants: small pores are better for oxalic acid (small molecule) and the opposite is observed for the reactive dye (large molecule).

The catalyst prepared by one-pot synthesis and all materials of cerium oxide supported on carbon xerogel presented better performance than the carbon xerogel in the ozonation of oxalic acid and the reactive dye.

The reaction mechanism is expected to involve the oxidation of the organic compounds on the catalyst surface, since the presence of a radical scavenger did not change, at least significantly, the kinetic results.

Among the studied materials, the sample with 1 wt% of cerium oxide prepared by one-pot synthesis was considered the best catalyst: in addition to its high catalytic activity, the preparation method is easier and less expensive.

Acknowledgments

This work was supported by project PEst-C/EQB/LA0020/2011 financed by FEDER through COMPETE. C.A.O. acknowledges the grant received from FCT (BD/45809/2008). The authors are indebted to Dr. Pedro Tavares (UTAD) for assistance with XRD analyses.

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